

# FERRO2003

## Fundamental Physics of Ferroelectrics

### Corrections

#### POSTER SESSION, FEBRUARY 3, 2003

POSTER SESSION	PRESENTATION ADDED	
P30	S. Koval, J. Kohanoff, R.L. Migoni and E. Tosatti	Ferroelectric instabilities and self-consistent mechanism for the isotopic substitution in KDP
P31	P. Yang, B.G.R. Burns and C.J. Gieske	The Origin of a Short-Range Interaction during a Ferroelectric Rhombohedral-Rhombohedral Phase Transformation

#### TUESDAY, FEBRUARY 4, 2003

The talk of Haydn Chen will be given by Eugene Colla.

SESSION 4	TALK ADDED	
17:10-17:25	J.C. Woicik	Site-specific x-ray photoelectron spectroscopy: A new method for measuring partial densities of valence states

# Ferroelectric instabilities and self-consistent mechanism for the isotopic substitution in KDP from first-principles

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We performed *ab initio* calculations to study ferroelectric instabilities and isotope effects in the H-bonded ferroelectric  $\text{KH}_2\text{PO}_4$  (KDP). The paraelectric (PE) phase is unstable with respect to a collective H ordering in the H-bridges, even keeping the K and P atomic positions fixed at their mean values of that phase. We demonstrate that the source of the ferroelectric (FE) instability is the hydrogen off-centering. This ordering, perpendicular to the tetragonal axis  $c$ , produces an electronic charge redistribution within the  $\text{PO}_4$  tetrahedral units, which polarize along  $c$ . Additional displacements of the P and K atoms reinforce the polarization. Cluster distortions following the H off-centered relaxation pattern in a mean-field PE phase, lead to instabilities which are significant only when the heavy ions P and K are also allowed to relax. The accurate description of the energetics achieved from first-principles, also allow us to conduct a first study of the nuclear quantum effects over the effective *ab initio* potentials and of the changes produced by isotopic substitution. Above certain cluster size, which is much smaller for DKDP, quantum mechanical calculations for the effective cluster mass yield energy levels below the intervalley barrier of the double-well cluster potential energy. Thus, cluster tunneling is allowed for distortions including heavy ions relaxations, with effective masses much larger than the total involved H or D mass. This explains the H double occupancy observed experimentally in the PE phase, and is also in agreement with the P-atom multi-site distribution detected experimentally in DKDP. Mass changes due to deuteration at fixed structural parameters cannot account for the huge isotope effect. However, the main effect of deuteration is a depletion of the proton probability density at the O-H-O center, which in turn weakens the proton-mediated covalency in the bridge. A lattice expansion follows then, which is coupled self-consistently with the proton off-centering. This self-consistent mechanism is illustrated with a non-linear model deduced from the *ab initio* calculations, and allows us to explain the huge isotope effect observed and the importance of geometrical effects proved by high-pressure experiments.

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**Site-specific x-ray photoelectron spectroscopy:  
A new method for measuring partial densities of valence states**

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X-ray photoelectron spectroscopy has emerged as a premier method for determining the electronic structure of solids or films. Unfortunately, as the intensity of a monochromatic photon beam is constant over the dimensions of the crystalline unit cell, standard photoemission measurements are unable to produce direct, site-specific valence information. However, such information is important for advancing our knowledge of how chemical bonding results in the solid-state electronic structure. Here we demonstrate that by utilizing the sinusoidal variation of the x-ray standing-wave interference field that results from the superposition of the incident and reflected x-ray beams in the vicinity of a crystal x-ray Bragg reflection, the photoelectron partial densities of states from the individual atoms of the unit cell may be directly obtained. The technique is demonstrated for GaAs and  $\text{TiO}_2$  and the results compared to state of the art, density functional calculations.

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# **The Origin of a Short-Range Interaction during a Ferroelectric Rhombohedral-Rhombohedral Phase Transformation**

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The origin of a short-range interaction developing in a high temperature rhombohedral ferroelectric phase as temperature approaches the phase transformation in the lead zirconate rich lead zirconate titanate solid solution is proposed. It is believed that the continued displacement of cations along the body diagonal direction with respect to oxygen planes during the cooling cycle induces the electrostatic interaction between large lead cation and the closest oxygen anions in the adjacent cells. As the distance between these ions gets closer and the electrostatic interaction increases, a structural instability develops, and eventually the material transforms into a low temperature rhombohedral structure. During this process the spontaneous polarization disengages from the thermal strain and couples with the oxygen octahedral rotation, as the perovskite unit cell doubles. The electrostatic nature of this short-range interaction during the structural phase transformation is demonstrated by the change of thermal mechanical properties, the spontaneous polarization development, the field-induced deformation behavior, and hydrostatic responses.

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